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Evaluation of mechanical soft-abrasive blasting and chemical cleaning methods on alkyd-paint graffiti made on carbonate stones

Dissertação para obtenção do Grau de Mestre em Conservação e Restauro

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Abstract

This study focuses on the assessment of three graffiti cleaning systems on alkyd-paint graffiti aerosols made on two Portuguese carbonate stones, a marble, *Branco*, and a limestone, *Lioz*. These carbonate stones are commonly used in Portugal as building materials and ornamental stones. Two non conventional commercial dry soft-abrasive blasting media (MC1 and MC2), specifically developed to clean the sensitive and delicate surfaces were tested, MC1 uses a sponge-like urethane polymer involving spherical calcium carbonate particles and in MC2 pure spherical calcium carbonate particles are used. An alkaline cleaner based on a solution of potassium hydroxide was also tested (CC1).

The criteria for assessing the effectiveness and potential risks included changes in the chromatic parameters, static contact angle and surface roughness of the stones, identification of deleterious products (i.e. salts) and modification of the morphology and the composition of the surfaces.

The methods were effective in the removal of the paint layers, although surfaces became slightly lighter. Adapting the classification proposed by Garcia and Malaga [29], the mechanical soft-abrasive cleaning methods were classified for both stones as Class C, i.e., with ΔEab near 12. The chemical cleaning was classified as Class A for marble stone ($\Delta Eab < 5$) and as Class B for the limestone ($5<\Delta Eab<10$). No sub-products were identified. With the chemical cleaning, distinct removal of crystals or dissolution of grain boundaries in addition to surface dissolution was observed.

The cleaning methods presented a slight low damage potential to these stone materials, i.e., the impact of the cleaning methods on the topography of the surfaces was much reduced. These methods also altered the water repellency of the stone surfaces. An increase in the static contact angles was observed and could be related with changes in the roughness of the surfaces and also to unremoved polymers absorbed in some of the pores of the surfaces.

Keywords: carbonate stones, graffiti, alkyd spray paints, chemical and mechanical soft-abrasive cleaning, effectiveness, harmfulness.

Publications: In the context of this dissertation several studies were developed resulting in submission and publication *"Evaluation of mechanical soft-abrasive blasting and chemical cleaning methods on alkyd-paint graffiti made on calcareous stones"* to Journal of Cultural Heritage. (http://dx.doi.org/10.1016/j.culher.2014.10.004)

Resumo

Este estudo avalia a eficácia de três métodos de limpeza de graffiti feitos à base de tintas alquidicas em aerosol. Tendo sido testados em duas surpefícies petreas calcárias portuguesas, o mármore Branco de Estremoz e o cálcario sedimentar Lioz de Pêro Pinheiro. Estas pedras calcárias são usualmente utilizadas como materais de construção bem como para fins ornamentais. Foram utilizados dois métodos de limpeza mecânica a seco (MC1 e MC2) com abrasivos especialmente desenvolvidos para limpeza de superfícies sensiveis e delicadas. MC1 utiliza uma esponja polimérica à base de uretano envolvendo micro partículas de carbonato de cálcio esfericas. MC2 utiliza apenas micro partículas de carbonato de cálcio convencionais. Um removedor químico de graffiti à base de hidróxido de potássio foi também testado (CC1).

Os critérios estabelecidos para definir a eficiência e riscos potenciais incluem a alteração dos parametros crómaticos, do ângulo de contacto estático, da rugosidade superficial das pedras, assim como a identificação de sub produtos (ex. sais) e a modificação da morfologia e composição das superfícies.

Os processos de limpeza testados mostraram-se foram eficientes na remoção das camadas cromáticas, apesar de as superfícies se terem tornado ligeiramente mais claras. Utilizando a classificação proposta por Garcia e Malaga [29], os métodos de limpeza mecânicos foram classificados como classe C para as duas tipologias pétreas, tendo sido alcançadas valores de ΔE^*ab próximo dos 12. O método de limpeza química foi classificado como classe A para o mármore ($\Delta E^*ab<5$) e Classe B para o Lioz ($5< \Delta E^*ab<10$). Não foram identificados sub produtos. Com a limpeza química foi observada a remoção de cristais ou dissolução nas fronteiras de grão para além da dissolução superficial.

Os métodos de limpeza utilizados representam ligeiro potencial de dano nos materiais petreos, i.e., o impacto dos mesmos na topografia das superfícies é muito reduzido. Estes métodos também alteraram a hidrofobicidade das superfícies. Observou-se um aumento do ângulo de contacto estático, podendo este, estar relacionado com alterações na rugosidade das superfícies, bem como de remoção incompleta dos polímeros de alguns poros das superfícies pétreas.

Palavras chave: Pedras carbonatadas, graffiti, tintas spray alquidicas, limpeza química e mecânica, eficiência, novcividade.

Publicações: No contexto desta dissertação foram desenvolvidos vários estudos resultando na submissão e publicação *"Evaluation of mechanical soft-abrasive blasting and chemical cleaning methods on alkyd-paint graffiti made on calcareous stones"* no Journal of Cultural Heritage. (http://dx.doi.org/10.1016/j.culher.2014.10.004)

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1. Introduction

Graffiti is an engraving, scratching, cutting or application of paint, ink or similar matter on the stone surface [1]. Graffiti is generally the result of an act of vandalism although some may have historical, aesthetical or cultural values and should be conserved. Graffiti media includes a wide range of materials such as paints applied by brushes (oils and synthetic resins) or aerosols (polyurethanes, lacquers and enamels), dyes, felt-tip markers, ball-point pens, wax and oil crayons and lipsticks, chalks, adhesive labels and posters and the physical scratching of surfaces [2], [3].

Graffiti, as an act of vandalism, is undoubtedly a major danger to stone Cultural Heritage and a risk for the preservation of the historical and cultural legacy for future generations. Graffiti can severely damage stone, accelerating its decay and lead to important materials losses and even to loss in value and significance [2], [3]. Moreover graffiti has also inevitable negative economic impacts to stone cultural heritage due to the impossibility to enjoy it adequately, and also to the necessity of adoption corrective measures, such as application of graffiti cleaning methods and preventive protection by using anti-graffiti coatings.

Graffiti cleaning is an essential part of conservation treatments and is not only necessary for aesthetical reasons but also required to ensure better preservation of stone materials. Although graffiti cleaning methods are potentially effective they present, in some cases, the potential for excessive material removal or other changes to the surfaces and, consequently, superficial, or even structural damage. Some graffiti cleaning methods/techniques can also accelerate stone decay through interaction with stone substrata or generation of by-products (e.g. soluble salts) which, remaining within the material, may affect the future preservation ([3], [4], [5]). In such cases irreversible damage happens to the surfaces which are unacceptable in objects with cultural heritage value. Other factors such as the nature, chemical, physical and mineralogical structure and physical condition of the stone material type of pre-existing soiling or patina present and type of graffiti marker should also be taken into consideration ([5], [6]).

Different techniques and methods have been studied and used to remove such unwanted marks such as those involving water jet, grit-blasting, chemical removal, laser technology and atmospheric plasma ([6]-[22]). The development of anti-graffiti protection/ barrier coatings intended to facilitate the removal of graffiti from the surfaces is also a subject of interest ([23]-[40]).

An understanding of the principles, effectiveness, harmfulness and nocivity of each cleaning method/technique and its comparison is thought to be essential for its conscientious use. Therefore this study focuses on the assessment of the effects of mechanical soft-abrasive blasting and chemical cleaning methods on alkyd-paint graffiti made on carbonate stones. In previous works were assessed the effects of these alkyd paint sprays in these stones when subjected to simulated graffiti situations in the laboratory [41], [42].

2. Materials and Methods

2.1 Materials description and characterization

Two Portuguese carbonate stones commonly used in Portugal as building materials and ornamental stones were chosen: a Cretacic limestone - *Lioz* and a Cambrian to Upper Silurian white marble - *Branco* (Fig. 2.1.). These materials have been widely used in monuments and are still used in the construction of modern buildings and sculptures not only in Portugal but also abroad.

Figure 2.1. - Investigated lithotypes: a) Lioz; b) Branco stones

Lioz is a coarse cream microcrystalline limestone, bioclastic and calciclastic, whereas *Branco* is crystalline calcite marble (~98% calcite), with a granoblastic texture with medium-grained zones. A detailed petrographical, chemical, physical and mechanical characterization of this limestone and marble is presented by [43] and [44], respectively. In spite of their different geological and petrographical characteristics, both lithotypes present very low porosity (<0.40%) and water absorption capacity (<0.15%) [45] their uniaxial compressive and flexural strength can be considered medium to high (>1000 kg.cm-2 and >200 kg.cm-2, respectively) [45].

The alkyd spray paints used in this work (Fig. 2.2.) correspond to trademarks MOTIP HOME & HOBBYLACQUER® [46]. The colours selected were gentian blue (RAL code R-5010), carmine red (R-3002) and jet black (R-9005). These sprays were chosen based on their low price and availability in non-specialized stores and their probable different interactions with stone substrata due to the use of different pigments, dyes or fillers. Details of the particular paint formulations are proprietary of the manufacturer and not available.

Figure 2.2. - Investigated lithotypes and alkyd sprays applied: jet black, carmine red and gentian blue paints.

Composition of these graffiti paints was characterized by Fourier Transform Infrared spectroscopy and the main component of these sprays is a polymeric base with different charges or fillers [42].

A set of twenty four parallelepiped test cupons (7 x 5 x 1.5 cm) were previously prepared for each lithotype (cutted using a circular diamond saw and finished using carborundum 180 and without any other surface finish). The cupons were uniformly sprayed with the alkyd paints (at an average angle of 45° and from a distance of 30cm, with environment conditions ranging between 18-25 ºC air temperature and 60-70% relative humidity), onto the surfaces in order to simulate the graffiti action [41]. The paints created a smooth, uniform and dense overcoat and filling in surface irregularities in both lithotypes [41]. A second set of samples, with the same geometry was left unpainted and considered as reference.

The cleaning tests were performed 24 months after the application of alkyd-spray paints.

2.2 Tested graffiti cleaning methods

Two non conventional commercial dry soft-abrasive blasting media, specifically developed to clean the sensitive and delicate surfaces (Fig. 2.3.), were used in this study: MC1 (Sponge-Jet ™) and MC2 (Exastrip ™). MC1 uses a sponge-like urethane polymer involving the abrasive composite (spherical calcium carbonate) whose function is to reduce dust levels and minimize abrasion of the substrate. In MC2 pure spherical calcium carbonate particles are used. To minimize dust, water can be added in MC2 system. The abrasive used in MC1 and MC2 was White SPOCC Sponge Media™ and EXAHDO® media, respectively. Besides the similar chemical composition of the particles their dimension is different: in MC1 technology the particles are smaller compared with those used with MC2 technology, i.e., particle's range varied between 27μm-100 μm and between 70μm-200 μm, respectively, as confirmed by scanning electron microscopy (Fig. 2.4.). Both technologies use low effective adjustable compressed air (from 0,5 to 2,5 bar), to propel the particles. In these experiments a maximum pressure of 2 bar was used, being the media amount and velocity tightly controlled to obtain the specified paint-removal and surface - profile results.

Figure 2.3. - Investigated lithotypes during cleaning of graffiti using the two mechanical dry soft-abrasive blasting media: a) MC1 and b) MC2.

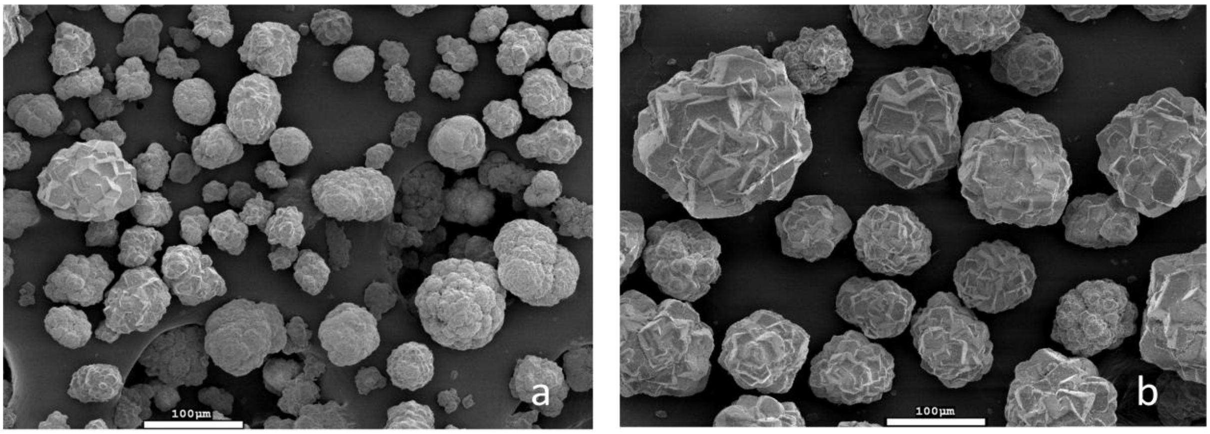

Figure 2.4. - FESEM images of spherical calcium carbonate particles: (a) MC1 and (b) MC2 technology.

Several aspects regarding health and safety issues and waste production must be mentioned when dealing with these soft-abrasive blasting cleaning methods. It is mandatory to encase the site carefully and the operators who work inside the shelter case must be protected from inhaling dust particles. Moreover they must use eye protection and also auricular protectors due to noise produced by the compressed air systems. The abrasive used in MC1 has the advantage of being able to be reused several times (four times maximum, according to the manufacturer) using a specific equipment for recycling.

Both blasting techniques have already been applied in the masonry cleaning of historical buildings such as the Wisconsin and Idaho state capitols, Washington Square Arch in New York, Mission San José y San Miguel de Aguayo in Texas, Notre Dame and Bercy Bridge in Paris [47]-[51].

A chemical method (CC1) based on a solution of potassium hydroxide (10–30% wt%) and surfactants (1-2% wt%, 2-aminoethanol) was also used (AGS 60™, Trion Tensid AB, Sweden). Potassium hydroxide is a suitable alkaline cleaner for acid sensitive historic masonry materials. This product was applied in two steps by soft brush on the stone wet surfaces and was leave to act for 30 minutes (1st step) + 15 minutes (2nd step) until paint graffiti was dissolved, followed by hot pressure tap water rinse (50°C) to increase the effectiveness of the alkaline cleaner for removing the graffiti spray paint. These samples were, then, dried and stored for 15 days in the laboratory environment (at 20 ± 2 °C air temperature and 60 ± 5% relative humidity). Also several aspects regarding health and safety issues must be mentioned when dealing with graffiti chemical removals, since they are potentially toxic and are often primary irritants of the skin, eyes and mucous membranes. So, it is recommend having good ventilation and the operators must use eye, airways and skin protections.

2.3 Methods

The criteria for assessing the effectiveness and potential risks of the studied cleaning systems included changes in the chromatic parameters, static contact angle and surface roughness of the stones, identification of deleterious products and modification of the morphology and the composition of the surface.

A stereomicroscope was used to record the sample surfaces before and after the application of the different cleaning methods. An Olympus system SZX12, mounted on an extendable arm SZ-STU2 with a digital camera DP-12 and an independent light source HighLight 3100 was used.

Field emission scanning electron microscopy (FESEM) was used to examine how topographical variations correlated to the removal of surface alkyd-paint materials. Moreover this tool was also used to evaluate compositional information of the surfaces. A Jeol JSM-7001F microscope equipped with an Oxford EDS light elements detector was used. The samples were previously coated with a high conductance thin gold-palladium film.

A Minolta portable spectrophotometer (model CM-508i) was used to monitor the effectiveness of the graffiti cleaning methods. Colour characterization tests were carried out with an integrating sphere (diffuse illumination /8º viewing angle), featuring an 8 mm diameter area of measurement with diffuse illumination by means of xenon flash arc lamp and 10 nm diffuse bandwidth. CIELAB values for D65 average daylight illuminant including ultraviolet radiation and CIE 2º Standard Observer following the ASTM-D2244-79/ D2244-85 standard method, was used [51]. Metric chroma (C*) was also calculated based on a* and b* values, as follows: $C^* = (a^{*2}+b^{*2})^{1/2}$.

Five measurements were averaged to obtain one data point.

The colour differences were determined as follows: $\Delta L^*=L^*1 - L^*0$; $\Delta a^*=a^*1 - a^*0$; $\Delta b^*=b^*1 - b^*0$, $\Delta C^*=C^*1 - C^*0$ where L*1, a*1, b*1, C*1 are the final values after cleaning, and L*0, a*0, b*0, C*0 are the reference ones, i.e., the original colour of the stones, prior to the application of spray paints. The total colour difference was also determined, using the following formula: $\Delta Eab = (\Delta L^{*2}+\Delta a^{*2}+\Delta b^{*2})^{1/2}$. García and Malaga proposed a classification based on ΔEab values as result of the application of an anti-graffiti product [29]. According to this classification, total colour changes cannot be seen by a human eye when ΔEab values are < 5 units (class A). When ΔEab values range between 5 and 10 units, then it can be assumed that the colour change can be perceived by a human eye but it is considered to be acceptable (class B). Finally, when ΔEab values are > 10 units, the colour change is considered clearly visible (Class C). Similar convention was adopted in this case-study.

Fourier Transform Infrared Spectroscopy (FTIR) was used to detect the presence of the red, blue and black paints and/or sub products generated by interaction of paints or cleaning methods with stone substrata. FTIR spectra were obtained in reference samples, in areas where graffiti paints were applied and also after the application of the mechanical soft-abrasive blasting and chemical cleaning methods. Micro samples were systematically collected from different areas using a steel scalpel. After cleaning, the surfaces were observed under a stereomicroscope and sampling corresponded to apparently cleaned areas. These micro samples were dried at 70°C (to eliminate the effect of water molecules) and powdered, before being dispersed in KBr pellets. Spectra were recorded with a Perkin Elmer Spectrum 65 spectrometer. For the 4000 cm^{-1} to 400 cm^{-1} region. Each data point was the result of the accumulation of 20 scans with a resolution of $2cm^{-1}$.

A surface roughness instrument (Surfecoder SE1200) was used to assess the morphological changes of the sample surfaces. Surface roughness is a physical characteristic of the surface texture and also an indicator of the impact of a cleaning method on the topography of the stone surfaces.

Parameters Ra, the arithmetic mean deviation of the roughness profile and Rz, the mean value of roughness depth of three consecutive sampling lengths, were evaluated. A scan length of 4 mm was used and the parameters were measured in triplicate for each sample at three different sampling points. It is very important to monitor variations on surface's roughness and to establish threshold values, in order to define the levels at which relevant parameters are likely to change surface roughness. Gaspar et al established damage thresholds based on variations of root mean square roughness (RMS) induced on surfaces after application of cleaning treatments based on the standard deviation of the RMS roughness values measured in reference sample surfaces before cleaning treatments [14]. A similar methodology was adopted in this case study based on Ra and Rz surface roughness parameters.

A goniometer (CAM 100, KSV, Helsinki, Finland) equipped with a digital camera and image analysis software was used to measure static contact angles. Static contact angles were measured in reference samples, in samples where graffiti aerosol paints were applied and after application of graffiti cleaning methods. Measurements were made at room temperature (20ºC) by applying the sessile drop method. Deionised water was used as the wetting liquid, with a droplet volume of 13 µL. Acquisition time was extended up to 17 seconds with a frame interval of 1s. Sessile drop contact angles of the air-water-substrate interface were measured four times in each sample.

3. Results and Discussion

3.1 Macroscopic observation and field emission scanning electron microscopy

The macroscopic observation of the stone surfaces after the application of the cleaning methods revealed they were apparently effective in the removal of the red, blue and black paint layers. The macroscopic observation of the stone surfaces after cleaning did not revealed relevant alterations of the surfaces. Apparently the outer layer of the stone material was not removed and cleaned areas did not looked different from the reference samples. Moreover no stone detachments or scaling were observed during the graffiti cleaning tests. Pathologies such as pitting, strong abrasion, microfissures or salt formation were not observed. Authors such as Young et al reported such pathologies in sandstone and granite building facades after cleaning those surfaces with mechanical soft-abrasive and chemical methods and related it to excessive pressure or dissolution of weaker spots in stone [53]. Ortiz et al also referred appreciable damage of the marble surfaces, i.e., surface erosion, after graffiti cleaning using pressurized water and UV pulsed laser ablation at 266 nm. Pressurized water and laser cleaning with 266 nm pulses originated multiple hues and loss of grains in the sub-millimeter scale. Nevertheless these authors did not observed structural damages after cleaning with chemical methods [17]. In addition Rivas et al also reported the formation of fractures on quartz crystals as response of Spanish granites to treatment with laser Nd:YVO4 removal of graffiti operating at a wavelength of 355 nm [18]. Antúnez et al evaluated different cleaning methods on graffiti made in a dolomitic marble and also reported superficial damage on the stone surfaces after application of high pressure water cleaning [8].

The stereomicroscope observation of the surfaces (Fig. 3.1.), revealed that soft-abrasive blasting and chemical cleaning were apparently effective in the removal of the red, blue and black paint layers, although some traces of paint were still visible. Nevertheless some differences were obtained for both lithotypes. *Branco*, the marble lithotype, presented a more homogeneous cleaned surface with only some sporadic small paint spots, whereas *Lioz*, the limestone, presented extra accumulation of the paint associated with heterogeneities of this stone like stilolytes. Ciliberto et al also observed some residues in the surface of limestone samples cleaned with commercial liquid and pasta cleaner products [26]. Moreover Lettieri et al and Antúnez et al also reported ineffective removal of an aerosol paint graffiti applied in a highly porous calcarenite [35] and in a dolomitic marble [8] after application of two chemical products (a glycol ether-based solution and a mixture of surfactants and solvents) and after application of high pressure water cleaning, respectively. Similar results were obtained by Liccheli et al i.e., the stone surfaces were still completely stained (with a permanent marker pen) after the cleaning step [30].

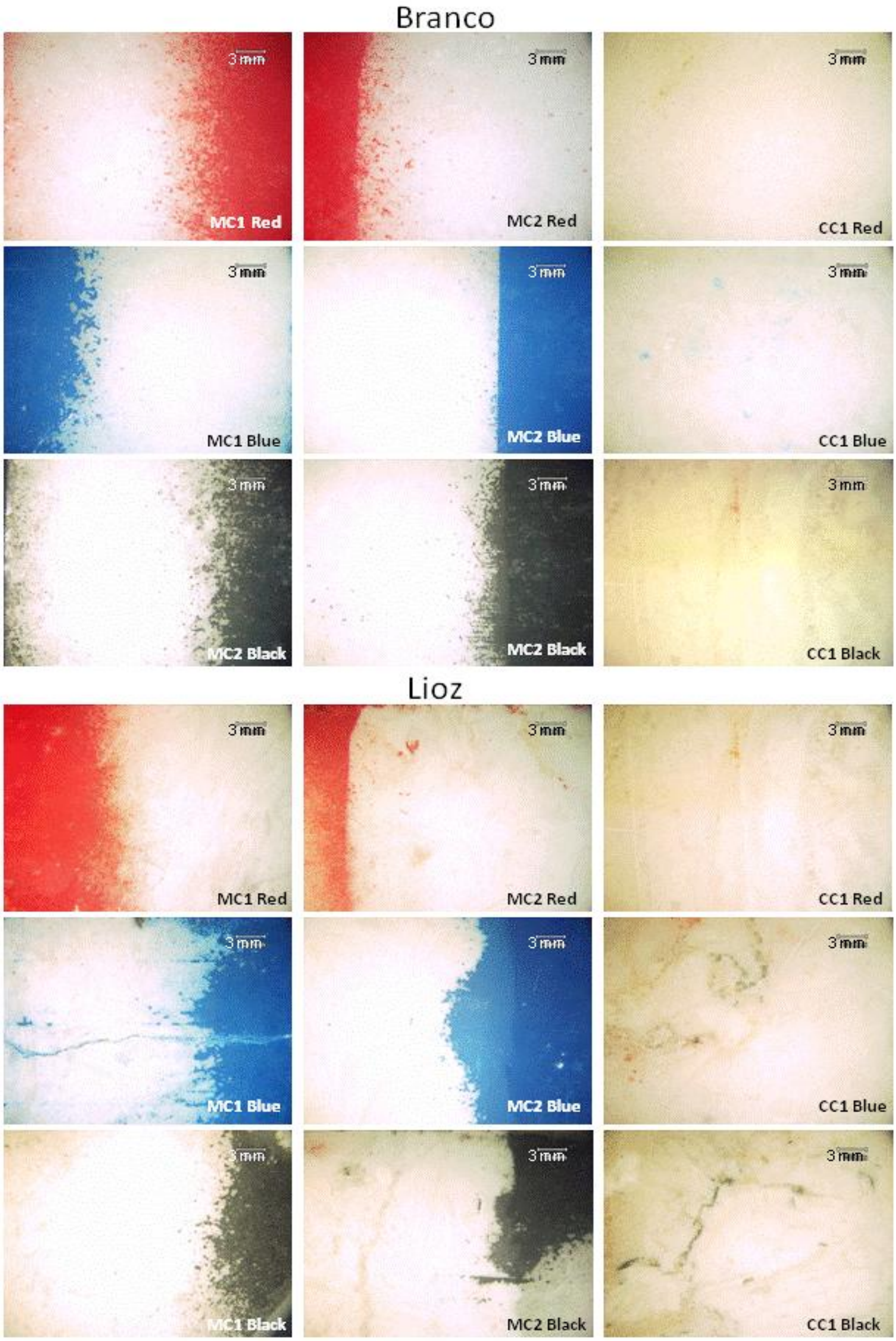

Figure 3.1. - Stereomicroscope images of the two lithotypes's surfaces after application of the tested graffiti cleaning methods.

Field emission scanning electron microscopy confirmed the composition and dimensions of the spherical precipitate of calcium carbonate particles used as abrasive in both blasting mechanical soft-abrasive cleaning systems (Fig. 2.4.).

Analyses of stone fragments after the application of the different cleaning methods using FESEM confirmed stereomicroscope observations, i.e., minimal or even non-existent paint remains on both stone surfaces independently on the cleaning method considered. Nevertheless, in what concerns surface modifications the extent and type were different. The extent of surface modifications was reduced when mechanical soft-abrasive blasting methods were applied, showing both stone surfaces slight erosion (Fig. 3.2. a, c, d and Fig. 3.3. a, c, d). This observation was in agreement with surface roughness values (Fig. 3.6.). Distinct removal of crystals (cleavage planes were visible), or dissolution of grain boundaries in addition to surface dissolution was observed after the application of the chemical cleaning method (Fig. 3.2.b and Fig. 3.3.b).

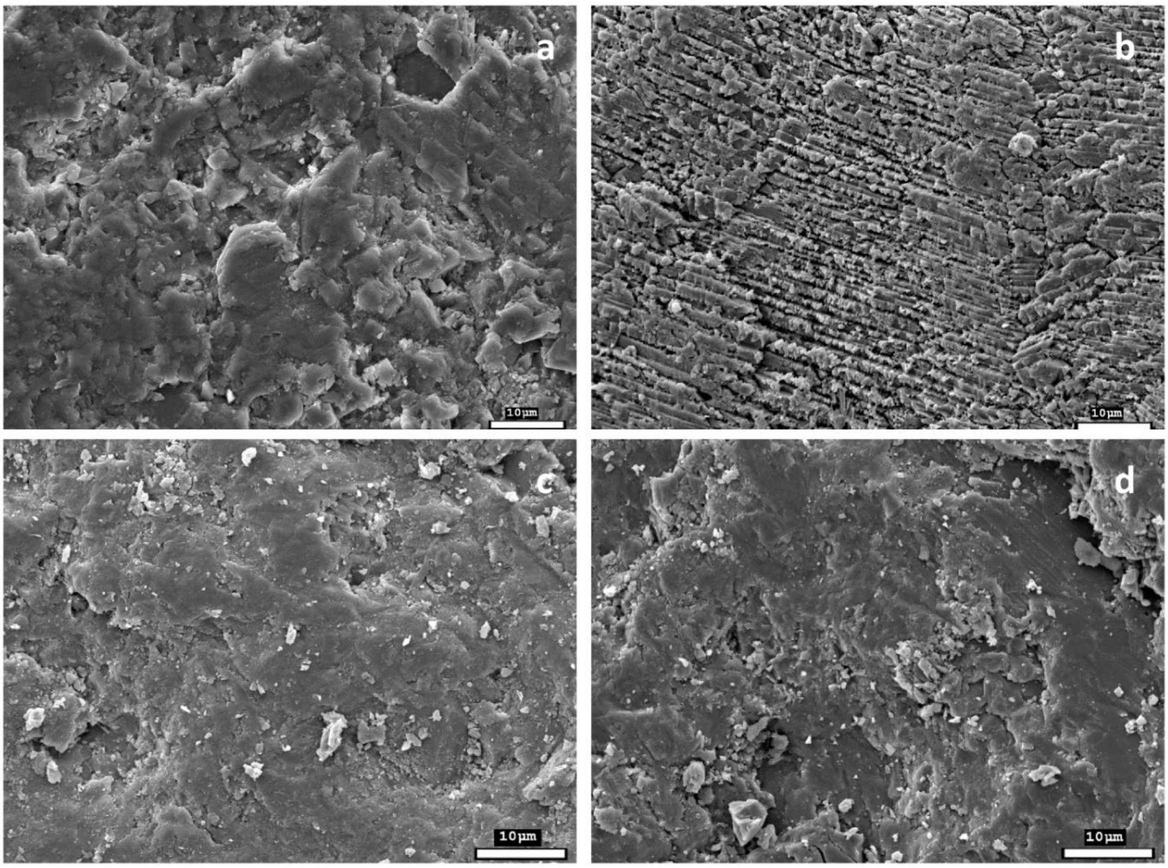

Figure 3.2. - FESEM images of Lioz: a) Reference sample (before paint application); b) after chemical cleaning; c) and d) after mechanical soft-abrasive cleaning with MC1 and MC2, respectively.

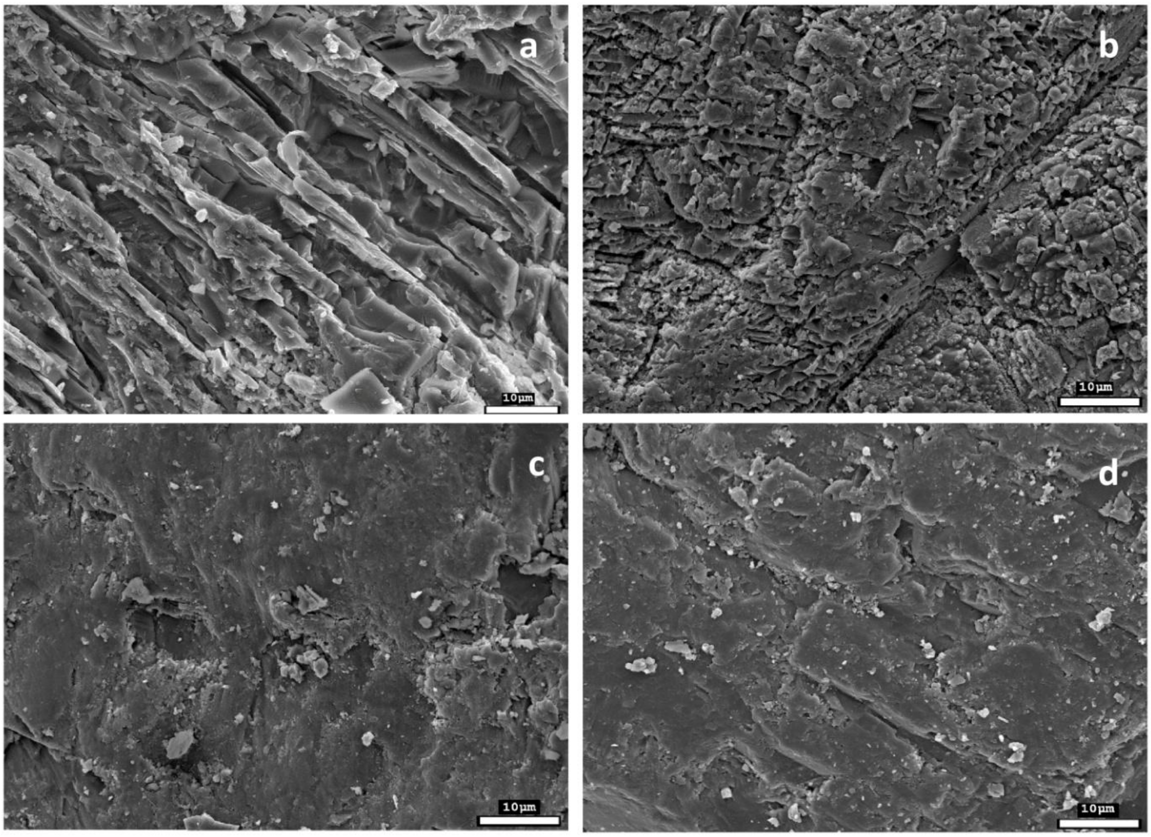

Figure 3.3. - FESEM images of Branco: a) Reference sample (before paint application); b) after chemical cleaning; c) and d) after mechanical soft-abrasive cleaning with MC1 and MC2, respectively.

3.2 Colorimetric assessment

The main colour changes induced by the tested graffiti cleaning methods were summarized in Table 3.1., Table 3.2. and Fig. 3.4. Similar tendencies were observed for both lithotypes and alkyd-paints applied. The cleaning methods mainly affected the L* coordinate and an increase in this value was observed. Average values of lightness between 80 and 85 were reached after cleaning *Branco* and *Lioz* surfaces, respectively (vs 70 and 75 in reference samples). The chroma (Cab) remained almost unaltered (Table 3.1., Table 3.2., Fig. 3.4.).

Table 3.1. - Mean values and standard deviations of the colorimetric differences (ΔL*, Δa*, Δb*, ΔCab) and of the global color changes (ΔEab) determined after cleaning of painted Lioz samples with the tested graffiti cleaning methods.

Lioz	Δ L*	Δ a*	Δ b*	Δ C_{ab}	Δ Eab
MC1					
carmine red	10.90 ± 1,50	1,00 ± 0,34	1,04 ± 0,16	1,38 ± 0,27	11,14 ± 1,45
jet black	10,70 ± 0,75	-0,30 ± 0,03	-0,89 ± 0,35	-0,92 ± 0,26	10,76 ± 0,68
gentian blue	6,29 ± 2,52	-3,83 ± 0,42	-6,78 ± 0,46	-1,36 ± 0,37	12,28 ± 3,93
MC2					
carmine red	11,36 ± 1,73	0,23 ± 0,52	1,15 ± 0,82	1,19 ±0,89	11,44 ± 1,68
jet black	10,45 ± 1,38	-0,37 ± 0,15	-0,18 ± 0,08	-0,24 ± 0,09	10,52 ± 1,41
gentian blue	13,23 ± 0,70	-0,45 ± 0,07	0,09 ± 0,27	-0,01 ± 0,34	16,31 ± 4,35
CC1					
carmine red	10,95 ± 2,47	-0,13 ± 0,00	-0,78 ± 1,62	-0,78 ± 1,59	11,03 ± 2,57
jet black	6,87 ± 0,77	-0,20 ± 0,09	0,58 ± 0,64	0,51 ± 0,62	6,90 ± 0,82
gentian blue	11,17 ± 0,40	-1,63 ± 1,33	1,17 ± 0,86	-1,40 ± 1,07	11,41 ± 0,12

Note: the colour differences correspond to the the final values after cleaning, and the reference ones, i.e., the original colour of the stones, prior to the application of spray paints.

Table 3.2.- Mean values and standard deviations of the colorimetric differences (ΔL*, Δa*, Δb*, ΔCab) and of the global colour changes (ΔEab) determined after cleaning of painted Branco samples with the tested graffiti cleaning methods.

Branco	Δ L*	Δ a*	Δ b*	Δ Cab	Δ Eab
MC1					
carmine red	9,84 ± 0,67	2,91 ± 0,86	-0,77 ± 0,61	0,83 ± 0,55	10,34 ± 0,62
jet black	10,13 ± 1,51	0,04 ± 0,24	-0,22 ± 0,50	-0,16 ± 0,48	10,14 ± 1,51
gentian blue	10,11 ± 0,83	-2,09 ± 0,88	-3,84 ± 1,62	1,95 ± 1,45	11,14 ± 0,74
MC2					
carmine red	11,41 ± 0,50	0,95 ± 0,41	-1,13 ± 0,45	-1,03 ± 0,38	11,52 ± 0,48
jet black	10,71 ± 0,77	-0,07 ± 0,40	-0,66 ± 0,47	-0,36 ± 0,28	10,74 ± 0,22
gentian blue	12,04 ± 1,26	-0,63 ± 0,15	-2,21 ± 0,99	-0,15 ± 0,67	12,29 ± 1,23
CC1					
carmine red	2,98 ± 0,25	1,02 ± 0,55	0,00 ± 0,17	-0,01 ± 0,14	3,19 ± 0,06
jet black	2,34 ± 0,52	0,18 ±0,07	1,84 ± 1,02	1,52 ± 0,62	3,04 ± 1,18
gentian blue	5,12 ± 1,43	-0,31 ± 0,00	-1,18 ± 0,32	-0,46 ± 0,14	5,26 ± 1,46

Note: the colour differences correspond to the the final values after cleaning, and the reference ones, i.e., the original colour of the stones, prior to the application of spray paints

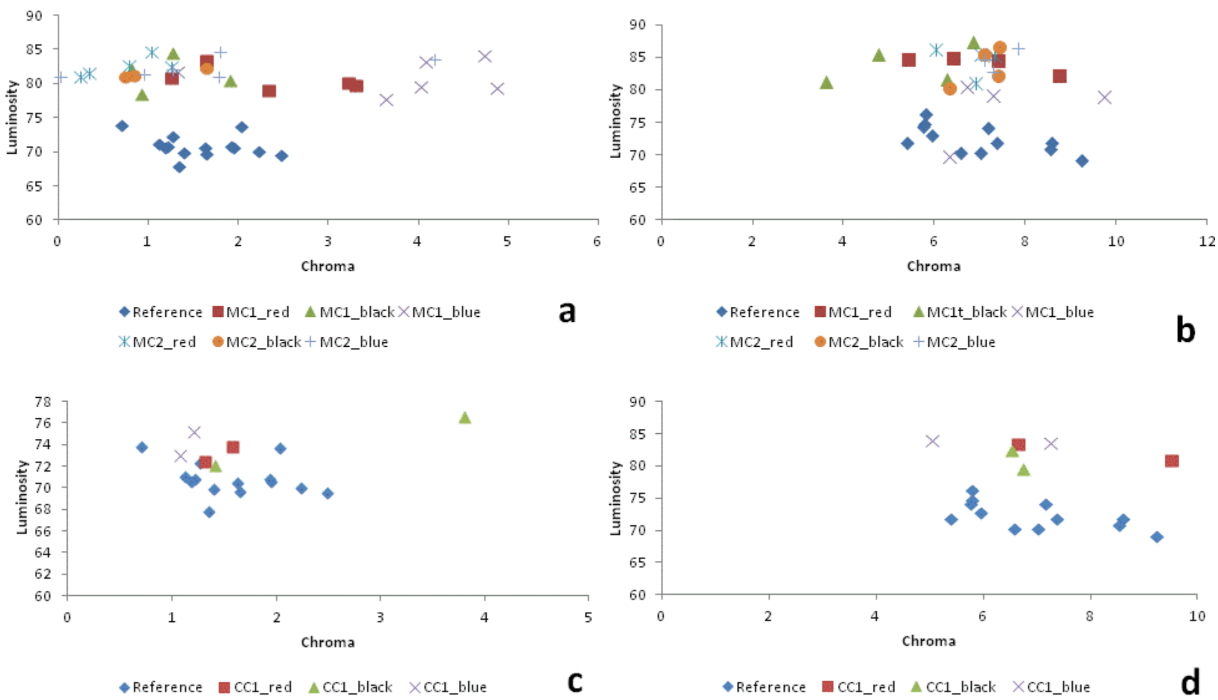

Figure 3.4. - Luminosity versus Chroma after mechanical soft-abrasive and chemical cleaning for Branco (a, c) and Lioz (b, d) lithotypes.

The average global colour changes (ΔEab) after cleaning both stone types, were significant, achieving ΔEab values above 10 (Table 3.1. and Table 3.2.). Exception was the chemical cleaning of marble samples (Table 3.2.).

Adapting the classification proposed by García and Malaga, the mechanical soft-abrasive cleaning methods were thus classified, for both stones, as Class C, i.e., the colour change was considered clearly visible [29]. Colour data suggested that the application of these mechanical soft-cleaning methods did affect the ultimate post-cleaning appearance of both lithotypes. Significative colour changes were also obtained by Ortiz et al and Rivas et al when evaluated laser cleaning methods on graffiti made on marble [17] and granite stones [18].

Regarding the chemical cleaning, two behaviors were observed. For the *Branco* marble, ΔEab values were lower than 5 units (Table 3.2.), i.e., the total colour changes could not be seen by a human eye. Therefore the samples after cleaning and the reference were colorimetrically similar. According to the former classification, the chemical cleaning of *Branco* marble was classified as Class A. For *Lioz*, the limestone, average ΔEab values were higher than 5 units (Table 3.1.) and in some cases higher than 10 units. It can therefore be assumed that the colour change can be perceived by a human eye but considered to be acceptable (5<ΔEab<10) or clearly visible (ΔEab>10). So, according to this classification the chemical cleaning method was classified as corresponding to Class B and Class C for *Lioz* limestone.

3.3 Fourier Transform Infrared Spectroscopy (FTIR)

The most representative FTIR spectra for reference samples of both lithotypes, for the alkyd-paints and for the surfaces after application of the cleaning methods are presented in Fig. 3.5.

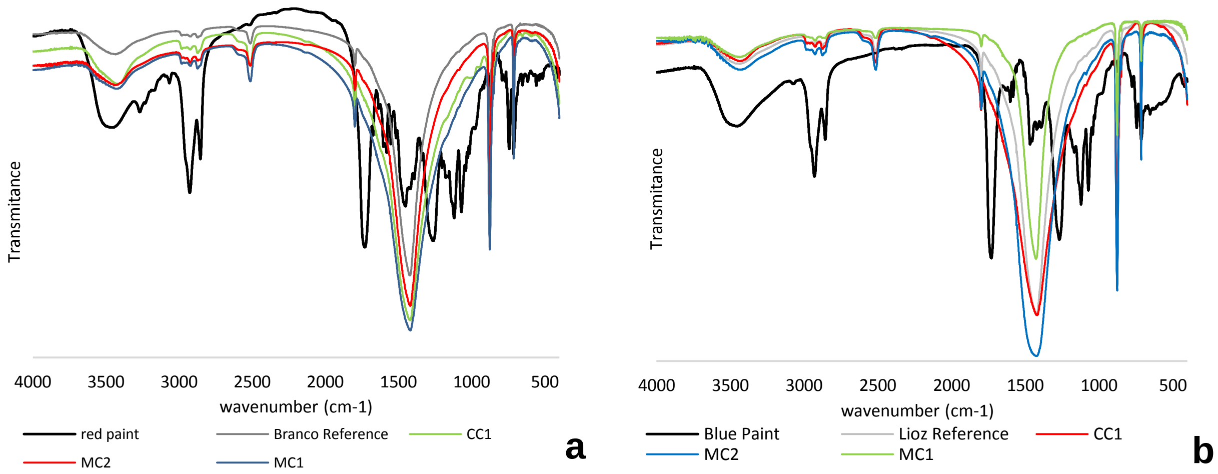

Figure 3.5. - Fourier transform infrared spectroscopy spectra (transmittance mode) of the reference samples and after mechanical soft-abrasive and chemical cleaning: *Branco* (a) and *Lioz* (b).

FTIR spectra indicate calcite as the main component of both lithotypes identified by its main absorption bands at 1424, 875 and 712 cm^{-1} (Fig. 3.5.). A strong band related to to the O-H stretching vibration of water was detected at around 3400 cm-1.

FTIR spectra confirmed the composition of red, blue and black paints, i.e, these paints are composed of alkyd and polyester resins (Fig. 3.5.) as previously demonstrated by Ribeiro [41]. The three paints are similar and the FTIR spectra presents bands assigned to C-H and ester functional groups. The bands around 2852cm^{-1} and 2923 cm^{-1} are assigned to C-H asymmetric stretching vibrations of alkanes. Esters were identified at 1729cm^{-1} corresponding to the stretching vibration C=O and those between 1300 and 1000cm^{-1} corresponding to COC group vibration stretching. Esters of unsaturated aliphatic fatty acids in the composition of the paints were identified by detection of an effect at 1260cm^{-1} and several effects around 1200–1100cm^{-1}.

According to the FTIR analyses, the chemical or mechanical soft-abrasive blasting cleaning achieved satisfactory results. Nevertheless in addition to the peaks characteristics of carbonates, weak but clear absorptions attributable to organic functional groups present in the paints spectra (Fig. 3.5.) were still present (Fig. 3.5.) and probably related to some residues retained by both stones after cleaning.

FTIR spectroscopy indicated the absence of sub products, i.e., no formation of salts were detected on the stone surfaces (Fig. 3.5.). Young et al considers that stone cleaning methods have the potential to cause accelerated stone decay through a variety of mechanisms namely chemical residues, when present, can cause salt related decay [52]. However in the present study no salt formation was identified.

3.4. Surface Roughness

Ra and Rz roughness parameters determined after cleaning of graffiti painted carbonate stones, as well as the reference values measured on the samples before graffiti simulation are presented in Table 3.3.

Table 3.3. - Ra and Rz roughness values determined after cleaning of painted carbonate surfaces as well as the reference values measured on the samples before graffiti simulation (values correspond to average ± SD).

	Lioz		**Branco**	
	Ra [μm]	**Rz [μm]**	**Ra [μm]**	**Rz [μm]**
MC1				
carmine red	2,863±0,928	17,087 ± 3,043	4,617 ±1,246	21,673±10,561
jet black	3,096±0,890	17,680 ± 7,269	5,075 ± 0,483	18,584 ± 1,935
gentian blue	2,758±0,909	11,024 ± 3,431	5,089 ± 1,217	23,301 ± 9,178
MC2				
carmine red	2,351±0,286	14,546 ± 3,742	4,199 ± 0,973	19,073 ± 8,048
jet black	2,385±0,270	13,458 ± 3,805	4,343 ± 0,555	16,003 ± 2,337
gentian blue	2,774±0,643	9,749 ± 1,451	3,948 ± 0,961	18,721 ± 8,268
CC1				
carmine red	1,506±0,529	6,500 ±1,820	3,182 ± 0,557	11,977 ± 2,008
jet black	2,656±0,930	9,809 ±3,186	3,560 ± 0,782	12,518 ± 1,821
gentian blue	1,769±0,878	8,405 ±5,178	2,157 ± 0,604	9,301 ± 1,873
Reference	**2,024±0,756**	**13,943 ± 4,261**	**4,159 ± 0,714**	**25,644 ± 3,594**

Although the chemical composition of these two materials is similar, they present very different structures, and thus a strong influence on the roughness values was observed. *Branco*, the crystalline stone, is rougher than *Lioz*, the sedimentary microcrystalline limestone (Table 3.3.).

For both stones and independently of the color applied to the stone surfaces, MC1 and MC2 (Fig. 3.6. a, b) induced a slight change (< 1 μm) of the arithmetic mean deviation of the roughness profiles. A decrease in Rz was observed for all studied situations and reductions of 1-10 μm were registered.

Alkaline chemical cleaning (CC1) induced, in both stones and for all spray colors applied, a slight reduction in roughness values (Fig. 3.6. c, d) with average variations less than 1 µm for Ra (for all colours). The most affected parameter was Rz, with a reduction of its values, which reached 13 µm in the case of red painted marble samples and 10 µm in the case of black painted limestone samples (in comparison with 26 µm and 14 µm in reference samples of *Branco* and *Lioz*, respectively). Antúnez et al also used chemical cleaning methods for graffiti removal and evaluated roughness parameters with laser scanning confocal microscopy [8]. In this study these authors reported significant roughness differences between cleaned and uncleaned zones, without specifying values. The cleaning of aerosol alkyd graffiti paints in both lithotypes induced a reduction in the Rz values by eliminating the relief associated with the mineral habit and therefore reducing the difference between peaks and valleys.

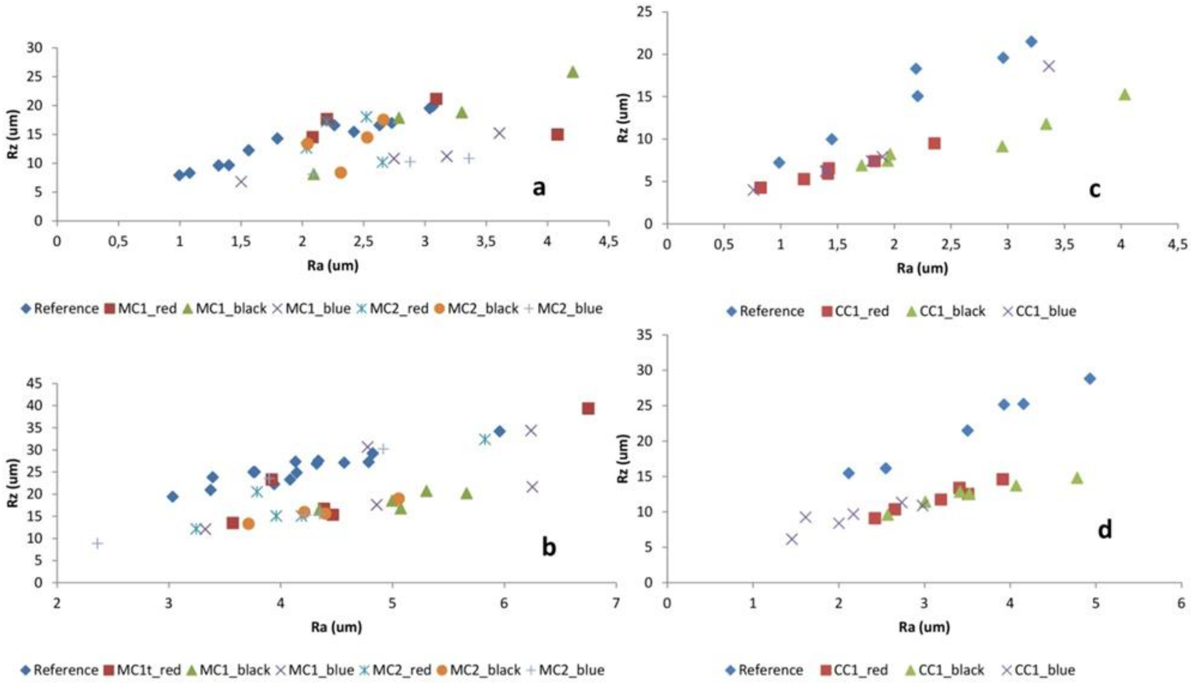

Figure 3.6. - Ra versus Rz values for reference surfaces and after mechanical soft-abrasive and chemical cleaning for Lioz (a,c) and Branco (b,d) surfaces.

In order to evaluate if roughness damage thresholds were exceeded with the graffiti cleaning methods, a methodology similar to the one proposed by Gaspar et al was applied [14]. Damage thresholds based on the standard deviation of the roughness values measured in reference samples before cleaning treatments was used. Thus, for *Lioz* damage thresholds were considered for variations of Ra and Rz values above 0,76 µm and 4,26 µm, respectively (Table 3.3.). For *Branco* damage thresholds were considered for variations of Ra and Rz values above 0,71 µm and 3,59 µm, respectively (Table 3.3.). Therefore if only Ra values were analysed one can considered there was no impact of cleaning treatments on surfaces. However based on Rz values the same cannot be inferred, i.e., these cleaning methods present a very slight damage potential to these stone materials.

3.5 Static Contact Angle

Fig. 3.7. and Fig. 3.8. display the static contact angles for both lithotypes before and after the application of the graffiti cleaning methods. Moreover reference values, corresponding to non-painted surfaces are also presented.

The *Branco* and the *Lioz* can be considered hydrophilic (θs<90º) before the application of aerosol-paint (Fig. 3.7. and Fig. 3.8.). Nevertheless marble is more hydrophobic than the limestone lithotype. This different behaviour can be related to their different intrinsic characteristics and also petrophysical properties.

Applying aerosol-paints over stone surfaces lead to an increase in the hydrophobic behaviour of both lithotypes, achieving static contact angles roughly 90° (Fig. 3.7. and Fig. 3.8.) and thus inducing enhancement in hydrophobicity, as already reported by [42]. The graffiti paint layers changed the stone surface's character from hydrophilic (θs<90º) to hydrophobic (θs>90º). Similiar results were obtained by Ciliberto et al after the application of orange, blue metal and red acrylic sprays in two Italian calcarenites [26]. Lettieri et al also reported an elevated hydrophobicity (water-stone contact angles higher than 120°) of the surfaces after the application of an orange aerosol spray paint on an Italian calcarenite [35].

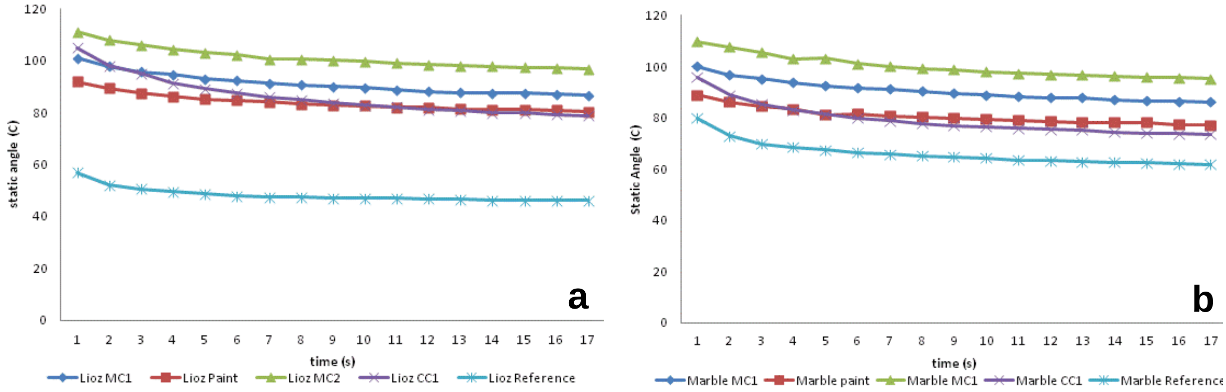

Figure 3.7. - Static contact angle values versus time for reference surfaces, after application of aerosol graffiti paints, after mechanical soft-abrasive and chemical cleaning on Lioz (a) and Branco (b) surfaces.

After the cleaning step, either mechanical blasting or chemical cleaning, and for both lithotypes an increase in the static contact angle values was observed (Fig. 3.7. and Fig. 3.8.). The cleaning methods particularly MC2 greatly modified static contact angles values. Average values of static contact angles of 111º and 110º were reached after cleaning *Lioz* and *Branco* surfaces respectively (vs 57º and 80º in reference samples). Nevertheless, MC1 and CC1 also induced static contact angles greater than 90º. The wettability was, therefore, drastically reduced and after cleaning both stone surfaces developed water repellency, meaning that the surfaces had become hydrophobic after cleaning. Ciliberto et al on contrary refer that after the application of chemical commercial cleaning products on acrylic graffiti made on some Italian calcarenites the contact angles were drastically reduced to values bellow 50° [26]. Moreover Lettieri et al also pointed out a reduction of the water-stone contact angle values and associated those values to unremoved paint from the surfaces [35].

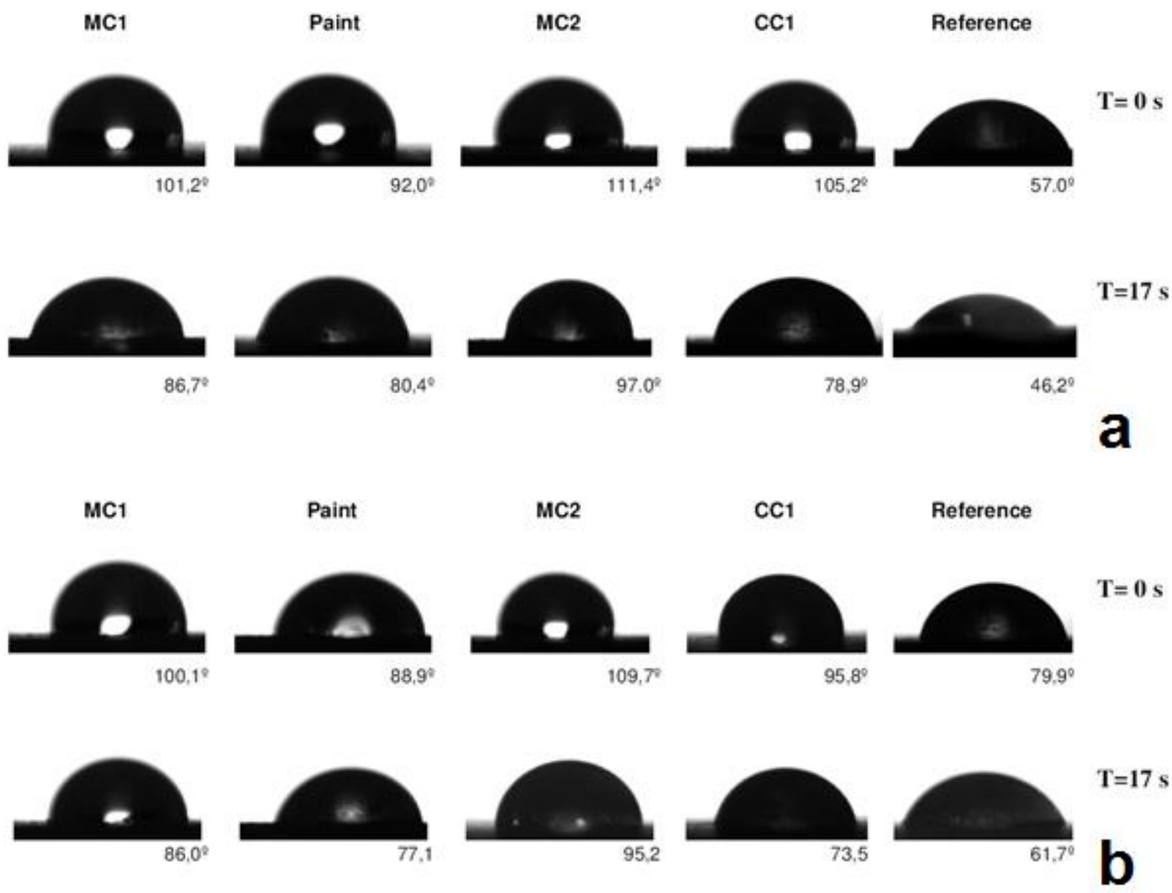

Figure 3.8. - Static contact angle images of 13 µL water droplet for time 0s and 17 s for reference surfaces, after application of aerosol graffiti paints, after mechanical soft-abrasive and chemical cleaning on the Lioz (a) and Branco (b) surfaces.

In order to justify the present unexpected data presented it is necessary to take into account the combined effect of roughness on static contact angle. In fact, the individual effects of heterogeneity and roughness on contact angles have been analysed in the literature by several authors such as [54] and [55]. In the present case a reduction in roughness (both Ra and Rz) was observed as result of the cleaning method, i.e., cleaning erased part of initial stone roughness and thus induced modification of static contact angles. Nevertheless it cannot be discarded the effects of unremoved polymers that can be absorbed in some of the pores of the surfaces. In fact remains of some paints were observed within some heterogeneities of the stones.

4. Conclusions

In the present study, the behavior of two non conventional commercial dry soft-abrasive blasting media and an alkaline cleaner on alkyd-paint graffiti aerosols made on carbonate stones was analyzed and discussed.

The criteria used for assessing efficiency and counter effects of the studied cleaning systems were changes in the chromatic parameters, static contact angle and surface roughness of the stones, identification of deleterious products and modification of the morphology and the composition of the surfaces. Microscopic and spectroscopic investigations performed on the cleaned samples revealed that both methodologies (mechanical soft-abrasive blasting and chemical cleaning) were apparently effective in the removal of the alkyd-paints, presenting both stones homogeneous cleaned surfaces. Nevertheless some traces of alkyd spray paint were still visible, mainly in *Lioz* stone, in areas associated with heterogeneities like stilolytes and fossils contours. Moreover very slight erosion of both stone surfaces were observed when mechanical soft-abrasive blasting methods were applied. In addition some removal of crystals, or dissolution of grain boundaries was also observed after application of the alkaline cleaner, which increased surface lightness, as confirmed by colorimetric measurements. All the cleaning methods tested increased the value of L*, i.e., after cleaning, both lithotypes became lighter than originally and the chroma (Cab) remained almost unaltered. The average global colour changes (ΔEab) after cleaning both stone types were slightly higher than 10 units, except chemical cleaning of marble samples (ΔEab close to 4 units).

The removal of alkyd paint graffiti from the *Lioz* and *Branco* with the tested cleaning methods did not induced formation of sub-products. Both cleaning methods (mechanical soft-abrasive blasting and alkaline chemical cleaning) presented a slight low damage potential to these stone materials, i.e., their impact on the topography of the surfaces was much reduced. The variations in Ra and Rz after cleaning were, for both lithotypes and for cleaning methods tested, bellow the damage thresholds established in reference sample surfaces.

Increase knowledge of the interaction of the alkyd spray graffiti cleaning methods with stone materials provides valuable insight and is thought to be essential for their conscientious use.

Bibliography

[1] ICOMOS-ISCS, Illustrated glossary on stone deterioration patterns, Champigny/Marne, ICOMOS International Scientific Committee for Stone (ISCS), 2008.

[2] M.E.Weaver, Removing Graffiti from Historic Masonry, Washington D.C., National Park Service– U.S Department of the Interior, 1995. (http://www.nps.gov/history/hps/tps/briefs/brief38.htm) (Accessed March 2013).

[3] M.J. Whitford, Getting Rid of Graffiti: A practical guide to graffiti removal and anti-graffiti protection, Spon Press, London, 1992.

[4] A.E. Grimmer, Keeping it Clean: Removing Exterior Dirt, Paint, Stains and Graffiti from Historic Masonry Buildings, U.S. Department of the Interior, National Park Service, Cultural Resources Heritage Preservation Services, 1988.

[5] G. Amoroso, V. Fassina, Stone decay and conservation- atmospheric pollution, cleaning, consolidation and protection, Elsevier, Amsterdam, 1983.

[6] D. Urquhart, The treatment of graffiti on historic surfaces- advice on graffiti removal procedures, anti-graffiti coatings and alternative strategies, Historic Scotland, 1999.

[7] S.E. Andriani, M.I. Catalano, G. Daurelio, A. Albanese, Marker and pen graffiti cleaning on diverse calcareous stones by different laser techniques, In Proc XVI International Symposium on Gas Flow, Chemical lasers and High-Power Lasers, Gmunden, Austria, september 2006 doi:10.1117/12.739334.

[8] V. Antúnez, P. Ortíz, J.M. Martin, A. Gómez, R. Ortíz, Evaluación de métodos de limpieza de graffiti en mármol, Macla; 16 (2012) 68-69.

[9] R. Butlin, C. Russell, I. McCaig, The removal of graffiti. In: Webster RGM, editor. Stone cleaning and the nature, soiling and decay mechanisms of stone, Donhead Publishing Ltd, London, 1992.

[10] S. Chapman, Laser technology for graffiti removal, J. Cult. Herit. 1 (2000) 575-578.

[11] J.R. Clifton, M. Godette, Performance tests for graffiti removers in Clifton: Cleaning stone and masonry, ASTM 1986 14-24.

[12] A. Costela, I. García-Moreno, C. Gómez, O. Caballero, R. Sastre, Cleaning graffiti on urban buildings by use of second and third harmonic wavelength of a Nd:YAG laser: a comparative study, Appl. Surf. Sci. 207 (2002) 86–99.

[13] M.P. Fiorucci, A.J. López, A.Ramil, S. Pozo, T. Rivas, Optimization of graffiti removal on natural stone by means of high repetition rate UV laser, Appl. Surf. Sci. 278 (2013) 268-272.

[14] P. Gaspar, C. Hubbar, D. McPhail, A. Cummings, A topographical assessment and comparison of conservation cleaning treatments, J. Cult. Herit. 4 (2003) 294–302.

[15] C. Gómez, A. Costela, I. García-Moreno, R. Sastre, Comparative study between IR and UV laser radiation applied to the removal of graffiti on urban buildings, Appl. Surf. Sci. 252 (2006) 2782–2793.

[16] I. Maxová, R. Slesinger, O. Kubova, Test of some anti-graffiti systems for preservation of sandstone monuments, 7th European Conference “SAUVEUR” SAFEGUARDED CULTURAL HERITAGE Understanding and Viability for the Enlarged Europe, Poster B-827-897, Prague, May 2006.

[17] P. Ortiz, V. Antúnez, R. Ortiz, J.M. Martín, M.A. Gómez, A.R. Hortal, B. Martínez-Haya, Comparative study of pulsed laser cleaning applied to weathered marble surfaces, Appl. Surf. Sci. 283 (2013) 193-201.

[18] T. Rivas, S. Pozo, M.P. Fiorucci, A.J. López, A. Ramil, Nd: YVO4 laser removal of graffiti from granite. Influence of paint and rock properties on cleaning efficacy, Appl. Surf. Sci. 263 (2012) 563–572.

[19] J. Penide, F. Quintero, A. Riveiro, A. Sanchez-Castillo, R. Comesan, J. delVal, F. Lusquiños, J. Pou, Removal of graffiti from quarry stone by high power diode laser, Opt. Laser Eng. 51 (4) (2013) 364-370.

[20] S. Siano, J. Agresti, I. Cacciari, D. Ciofini, M. Mascalchi, I. Osticioli, A. Mencaglia, Laser cleaning in the conservation of stone, metal, and painted artifacts: state of the art and new insights on the use of the Nd:YAG lasers, Appl. Phys. A-Mater. 106 (2) (2012) 419–446.

[21] E.M. Winkler, Stone in Architecture: Properties, Durability, Springer-Verlag Berlin, 1997.

[22] S. Voltolina, C. Aibéo, T. Cavallin, E. Egel, M. Favaro, V. Kamenova, L. Nodari, A. Pavlova, I. Pavlova, S. Simon, P. Scopece, E.V. Falzacappa, A. Patelli, Assessment of atmospheric plasma torches for cleaning architectural surfaces, in Built Heritage 2013, Monitoring Conservation Management, Milan, November 2013 1051-1057.

[23] J. Ashurst, N. Ashurst, Practical Building Conservation, English Heritage Technical Handbook, Volume I – Stone Masonry, Gower Technical Press, London, 1998.

[24] P.M. Carmona-Quiroga, R. Fort, Valuation of the effectiveness of an anti-graffiti product applied to “Blanco Paloma” limestone, in Heritage, Weathering and Conservation Conference HWC2006, Madrid, June, 2006, 785-789.

[25] P.M. Carmona-Quiroga, S. Martínez-Ramírez, S. Sánchez-Cortés, M. Oujja, M. Castillejo, M.T. Blanco-Varela, Effectiveness of antigraffiti treatments in connection with penetration depth determined by different techniques, J. Cult. Herit. 1 (2010) 297–303.

[26] E. Ciliberto, D.M. Battaglia, C. Capello, M. Gatto, S. La Delfa, M. Masieri, G. Quarta, Graphic Vandalism: study of the interaction of spray varnishes with stone materials and test of some antigraffiti treatments, Procedia Chem. 8 (2013) 165 – 174.

[27] G. Gardei, O. Garcia, M. Riedl, I. Vanhellemond, J. Strupi Suput, M.L. Santarelli, I. Rodríguez-Maribona, U. Müller, Performance and Durability of a New Antigraffiti System for Cultural Heritage – The EC Project GRAFFITAGE. in 11th International Congress on Deterioration and Conservation of Stone, Torun, September 2008, 889-897.

[28] O. García, I. Maribona, A. Gardei, M. Riedl, Y. Vanhellemont, M.L. Santarelli, J. Strupi Suput, Comparative study of the variation of the hydric properties and aspect of natural stone and brick after the application of 4 types of anti-graffiti, Materiales de Construcción 60 (2010) 69-82.

[29] O. García, K. Malaga, Definition of the procedure to determine the suitability and durability of an anti-graffiti product for application on cultural heritage porous materials, J. Cult. Herit 13(1) (2012) 77–82.

[30] M. Licchelli, S.J. Marzolla, A. Poggi, C. Zanchi, Crosslinked fluorinated polyurethanes for the protection of stone surfaces from graffiti, J. Cult. Herit. 12 (1) (2011) 34–43.

[31] B. Lubelli, R.P.J. van Hees, T.G. van de Weert, The drying behavior of building materials treated with anti-graffiti, in 5th International Conference on water repellent treatment of building materials, Brussels, April 2008, 85–94.

[32] K. Malaga, K. Mueller, Relevance of hydrophobic and oleophobic properties of anti-graffiti systems on their cleaning efficiency on concrete and stone surfaces, J. Mater. Civ. Eng. 25(6) (2013) 755-762.

[33] K. Manczyk, K. Manczyk, B. Trzebicka, A. Dworak, Anti-graffiti protective coating, Polimery-W 53 (2008) 830–835.

[34] B. Meng, U. Mueller, O. Garcia, K. Malaga, Performance of a New Anti-Graffiti Agent used for Immovable Cultural Heritage Objects, Int. J. Archit. Herit. 8 (2014) 820-834

[35] M. Lettieri, M. Masieri, Surface characterization and effectiveness evaluation of anti-graffiti coatings on highly porous stone materials, Appl. Surf. Sci. 288 (2014) 466-477.

[36] U. Müller, K. Malaga, A. Gardei, Study on the application of anti-graffiti systems on natural stones and concrete, in 6th International Conference on water repellent treatment of building materials, Rome, May 2011, 167-180.

[37] S. Saïdi, F. Guittard, S. Geribaldi, Polymères contre graffiti, Actual. Chim. 240 (2001) 3 – 14.

[38] A. Tarnowski, Polysaccharide anti-graffiti coating as a preventive conservation coating on sandstone and marble, in 10th International Congress on Deterioration and Conservation of Stone, Stockholm, June 2004, 383-390.

[39] M. Zielecka, Antigraffiti protection of porous building materials, Double Liaison, 517 (2000) 55–58.

[40] A. Zielnik, Durability: the art of graffiti prevention, JAC 1(4) (2005) 70–74.

[41] A. Dionísio, T. Ribeiro, When graffiti is not art: the damage of alkyd sprays on calcareous stones employed in Cultural Heritage, In: Frediani P, Frediani M and Rosi, (eds), Cultural Heritage: protection, developments and international Perspectives (Focus on Civilizations and Cultures), Nova Science Publishers; 2013, 279-291 (e-book ISBN: 978-1-62808-822-9).

[42] T. Ribeiro, A. Dionísio, L. Aires-Barros, Aerosol-Paint Graffiti: the effects on calcareous stone, Int. J. Rest. Build. Mon., 15 (1) (2009) 51-56.

[43] P. Figueiredo, L. Aires-Barros, The Lioz: the natural stone of Lisbon. In: Proc II Congreso Int. de la Piedra, Madrid, Spain, May 1998 (CD-ROM).

[44] L. Lopes, R. Martins, Marbles from Portugal: http://www.naturalstone-online.com/fileadmin/Naturstein Daten/Anzeigenseite_neu/portugal_marble1.pdf (accessed March 2014).

[45] http://rop.ineti.pt/rop/FormTipo.php

[46] Motip Home Page. www.motip.com (accessed March 2014)

[47] J. Correia, F. Matero, Calcium tartrate tetrahydrate preconsolidation of salt-contaminated limestone at Mission San José y San Miguel de Aguayo, J. Am. Inst. Conserv. 47 (2) (2008) 81-95.

[48] M.L. Danner, Capitol idea, Building Design Construction 2010 39-40.

[49] L. Lavelle, Soft Option: Contemporary technology turns back the clock at the Marion County Courthouse in West Virginia, Traditional Building, 2007 135-136.

[50] J. Maty, Projects: Paint Removal, AC, 2007, 11-13.

[51] M. Rabinowitz, R. Gerstad, "Let Us Raise a Standard..." The Preservation of Washington Square Arch in New York City, APT Bulletin 36 (2/3) (2005) 47-55.

[52] ASTM D2244/D2244-85 Standard Practice for Calculation of Color Tolerances and Color Differences from Instrumentally Measured Color Coordinates.

[53] M.E. Young, D.M.C. Urquhart, R.A. Laing, Maintenance and repair issues for stone cleaned sandstone and granite building facades, Build. Environ. 38 (9-10) (2003) 1125-1131.

[54] G. Wolansky and A. Marmur, Apparent contact angles on rough surfaces: the Wenzel equation revisited, Colloids Surf., A 156 (1999) 381-388.

[55] T.S. Meiron, A. Marmur, I.S. Saguy, Contact angle measurement on rough surfaces, J. Colloid Interface Sci. 274 (2) (2004) 637-644.